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18. SUPPLEMENTARY NOTES

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Nitramines from tert-Amines.
α-Substitution in Nitramines.
Cyclic Nitronic-Carboxylic Acid Anhydrides.
Nitroform and Isocyanides, Products from.
Nitropyrroles, Peview of.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A general procedure for the preparation of nitramines from tert-amines was developed. The best procedure calls for an initial transformation of the tertiary amine into a nitrosamine followed by oxidation to the nitramine.

From tri-n-butyl amine and nitric and hydrochloric acids in acetic anhydride, di-n-butylnitrosamine was reproducibly obtained (60%). Other examples are discussed. Nitrosamines are routinely

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oxidized to nitramines in nearly quanititative yields.

Conversion of a carboxyl into an amino group afforded 1-nitro-2-aminopiperidine isolated as either its carbamate or urea derivative. This result has encouraged the exploration of α-aminonitramines (or selected derivatives) in synthesis of dense fused ring systems (cage compounds).

Cyclic nitronic-carboxylic acid anhydrides is a thesis research area for a graduate student. A five membered and a six-membered (not confirmed) example have been prepared. An acyl derivative of the former readily polymerized, as expected, by spontaneous ring opening. The work is continuing.

Sydnones are energetic compounds available from certain aryl isocyanides and nitroform. This new reaction was discovered by an undergraduate research student. A report for publication is in preparation.

Nitrolys of CN Single Bonds and Chemistry of Nitro and Nitroso Groups.

Progress on Five Projects.

I. Project Titles and Goals.

A. Nitramines from Tertiary Amines. Sparse information scattered throughout the literature was to be organized and a general procedure developed.

B. α-Substituents in Nitramines. An exploratory survey of functional group interchange at the α-position of nitramines was undertaken.

C. Cyclic Nitronic-Carboxylic Acid Anhydrides. Nitro derivatives of five- and six-membered ring examples of these rarely encountered molecules were sought for evaluation as monomers for polymeric binders.

D. Products from Nitroform and Isocyanides. Further investigation on a recently discovered reaction was proposed to evaluate the potential preparation of energetic materials, e.g., nitromesoionic heterocycles.

E. Nitropyrroles. A thorough review of the literature on nitropyrroles was undertaken.

II. Project Summaries.

A. Nitramines from Tertiary Amines. The nitronium cation converted tertiary amines 1 to nitrosamines 4 which were oxidized to nitramines 5. Certain exceptional examples directly gave nitramines 5 rather than nitrosamines 4; these correlated with the dissociation of a stable carbonium ion, e.g., $R_3\overset{+}{C}$, rather than an elimination of nitrous acid from an intermediate quaternary nitrammonium ion 2a,b. The reactions are discussed and examples given.

$$R_2NCH_2R \xrightarrow{NO_2^+} R_2\overset{+}{N}(NO_2)CH_2R \xrightarrow{-HNO_2} R_2\overset{+}{N}{=}CHR$$

1 2a 3

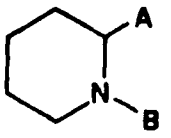
$$3 \xrightarrow[-RCHO]{HONO} R_2NNO \xrightarrow{[O]} R_2NNO_2$$

4 5

$$R_2\overset{+}{N}(NO_2)-CR_3 \longrightarrow R_2NNO_2 + R_3C^+$$

2b

B. α-Substituents in Nitramines. α-Pipecolinic acid 6a was converted to 1-nitro-2-piperideine 7 via the isolated intermediates: 1-nitropiperidine-2-carboxylic acid 6b, azide 6c, 1-nitropiperidine-2-isocyanate 6d, and methyl 1-nitropiperidine-2-carbamate.



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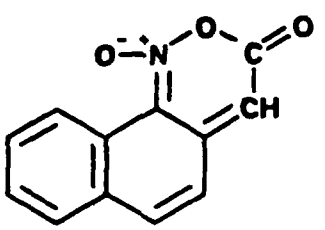
	A	B
a	CO_2H	H
b	CO_2H	NO_2
c	CON_3	NO_2
d	NCO	NO_2
e	$NHCO_2CH_3$	NO_2

7

C. Cyclic Nitronic-Carboxylic Acid Anhydrides. The anhydrides 8 and 9 have been prepared. The latter and its easily obtained polymer 10, a liquid, have the calculated density of 1.9.



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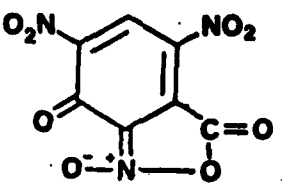

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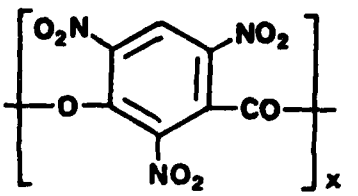

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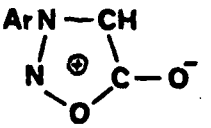
D. Products from Nitroform and Isocyanides. From aryl isocyanides 11 and nitroform 12 sydnones 13, related aromatic amines, and unknown products were obtained.

ARNC
11

$HC(NO_2)_3$
12



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III. Project Progress Reports.

A. Nitramines from tertiary amines.

1. Introduction. An efficient conversion of a tertiary aliphatic amine 1 to a dialkylnitrosamine 4 by treatment with nitric acid has been elucidated and developed. When followed by any of the several known oxidations of nitrosamines an additional route to nitramines 5 became available.

R_2NCH_2R R_2NNO R_2NNO_2

1 4 5

2. Background. Prior to this work there were scattered reports of tertiary amine conversions to nitramines with nitrolysis of hexamethylene tetramine to RDX and HMX being the best

known example.[1-3] In the generally accepted explanation for this reaction of a gem-diamine 14 a combination with a nitronium cation to give initially an N-nitroammonium cation 15 was proposed.[4] A dissociation then afforded a nitramine 5 and an α-aminocarbenium cation 16. Stability of the cation 16 favored this dissociation over other conceivable fates of the cation 15.

$$\underset{\underline{14}}{R_2NCH_2NR_2} + NO_2^+ \rightleftharpoons \underset{\underline{15}}{R_2NCH_2\overset{+}{N}R_2}\Big|_{NO_2}$$

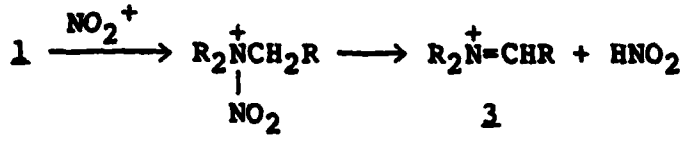
$$\underline{15} \rightleftharpoons \underset{\underline{16}}{R_2N\overset{+}{C}H_2} + \underline{5}$$

Attempts to extend the nitrolysis reaction to other tertiary amines met with minimal success[2] except for certain isolated examples,[3] each of which depended on the breakdown of a nitrammonium cation into a stable carbenium cation. This was recently demonstrated in the nitrolysis of dimethyl tert-butyl amine 17 to dimethyl nitramine 5 (R = CH_3).[5] The simultaneous formation of a trace amount of tert-butylmethylnitrosamine 18 furnished a clue for an important alternative breakdown of the nitrammonium cation 15. This competitive reaction has afforded a general method for the conversion of a tertiary aliphatic amine to a dialkylnitrosamine.

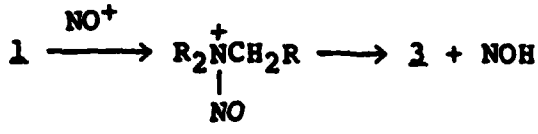
$$\underset{\underline{17}}{(CH_3)_2NC(CH_3)_3} \xrightarrow[(CH_3CO)_2O]{HNO_3} \begin{cases} \xrightarrow[15\%]{} \underline{5}\ (R = CH_3) + (CH_3)_3C^+ \\ \xrightarrow{} CH_3N(C(CH_3)_3)NO + [CH_2O] \\ \qquad \underline{18}\ \text{trace} \end{cases}$$

A proposed elimination of nitrous acid from a nitrammonium

cation 2a is analogous to the similar elimination of nitroxyl from nitrosammonium cation intermediates 19 in the conversion of tertiary aliphatic amines to dialkylnitrosamines by nitrous acid.[6]



2a



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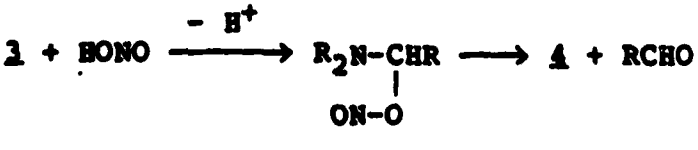
There is also a similarity with an elimination of nitrous acid from an o-nitrosohydroxylammonium cation intermediate 20 in the conversion of a tertiary amine oxide 21 to a nitrosamine 4 by treatment with a nitrosating agent.[7]

21 20

In each of these last three reactions the intermediate immonium cation 3 combined with nitrous acid (or other nitrosating agent, if present) to produce a nitrosamine 4 and a carbonyl compound via a proposed nitrite ester 21.



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3. Results. Initial development of this preparative method for nitrosamines was brought about by investigating N,N-dimethylbenzyl amine 22,[8] N,N-dimethyldibenzyl amine 24,[8] triethyl amine 25,[8] and tri-n-butylamine 26.[8]

$C_6H_5CH_2N(CH_3)_2$ (22) $C_6H_5CH_2CH_2N(CH_3)_2$ (23) $(C_6H_5CH_2)_2NCH_3$ (24)

$(C_2H_5)_3N$ (25) $(CH_3CH_2CH_2CH_2)_3N$ (26)

Nitronium tetrafluoroborate either in various organic solvents or in concentrated sulfuric acid efficiently nitrated the aromatic rings in amines 22 and 23.[10] From the reaction of 23 in sulfolane a trace of dimethylnitramine 5 (R = CH_3) was also detected. As expected, ring nitration was also brought about by a mixture of concentrated nitric and sulfuric acids and by a mixture of nitric and perchloric acids.

A mixture of the amine 22, nitric and hydrochloric acids in acetic anhydride[11] brought about the formation of benzylmethylnitrosamine 27 and benzaldehyde 28. It was presumed that undetected formaldehyde accompanied the formation of product 27 and that undetected dimethylnitrosamine 4 (R = CH_3) accompanied the formation of product 28. A redox reaction between nitric and hydrochloric acids [12] produced dinitrogen trioxide, a nitrosating agent for the intermediate formation of the nitrite ester 21. Acetyl nitrate[13] and nitrite[14] were probably present; however, their contribution to product formations was not determined.

$$\underline{22} \xrightarrow[\text{HCl (3 mol)}]{\text{70\% } HNO_3 \text{ (2 mol)}} C_6H_5CH_2NCH_3 + [CH_2O] + \underline{22}$$
$$\underset{\text{NO}}{|} \qquad\qquad 36\%$$
$$(CH_3CO)_2O \text{ (10 mol)} \qquad \underline{27} \quad 84\%$$
$$\text{15 m at } 50^\circ\text{, 16 h at } 25^\circ$$

$$\underline{22} \xrightarrow[\text{excess dry HCl gas}]{\text{100\% } HNO_3 \text{ (2 mol)}} \underline{27} + C_6H_5CHO + [CH_2O + (CH_3)_2NNO]$$
$$(CH_3CO)_2O \text{ (10 mol)} \quad 26\% \quad \underline{28} \quad 69\%$$
$$\text{16 h at } 25^\circ$$

$$2\ HCl + 2\ HNO_3 + 3\ (CH_3CO)_2O \rightleftharpoons 2\ CH_3COCl + N_2O_3 + 4\ CH_3CO_2H$$

$$CH_3COCl + N_2O_3 \rightleftharpoons CH_3CO_2NO + NOCl$$

A similar treatment converted dibenzyl methyl amine 24 to the nitrosamine 27 and benzaldehyde 28. Diethyl nitrosamine 4 (R = C_2H_5) was obtained from triethyl amine 25.

$$\underline{24} \xrightarrow[\text{HCl (3 mol)}]{\text{90\% } HNO_3 \text{ (2 mol)}} \underline{27} + \underline{28}$$
$$(CH_3CO)_2O \text{ (10 mol)} \quad 64\% \quad 34\%$$
$$\text{50 h at } 25^\circ$$

$$\underline{25} \xrightarrow[\text{HCl (3 mol)}]{\text{70\% } HNO_3 \text{ (2 mol)}} \underline{4}\ (R = C_2H_5)$$
$$(CH_3CO)_2O \text{ (10 mol)} \quad 32\%$$
$$\text{0.5 h at } 50^\circ\text{, 16 h at } 25^\circ$$

Tri-n-butylamine 26 was converted to di-n-butylnitrosamime 4 (R = $CH_3CH_2CH_2CH_2$) in 62% yield by similar treatment with nitric and hydrochloric acids in acetic anhydride. On repeating the reaction without hydrochloric acid the yield was 47%. In the latter example the presence of the nitrosating agent depended on the breakdown of the intermediate nitrammonium cation 2a.

$$\underline{26} \xrightarrow[\text{HCl (3 m)}\\ (CH_3CO)_2 \text{ (10 m)}\\ \text{0.5 h at } 50^\circ\text{, 16 h at } 25^\circ]{\text{70\% } HNO_3 \text{ (2 m)}} (n\text{-}C_4H_9)_2NNO \quad 62\%$$

$$\underline{26} \xrightarrow[(CH_3CO)_2O \text{ (10 m)}]{\text{100\% } HNO_3 \text{ (3 m)}} (n\text{-}C_4H_9)_2NNO \quad 47\%$$

References

A-1. G.F. Wright, "Methods of Formation of the Nitramino Group and its Properties and Reactions," in "The Chemistry of the Nitro and Nitroso Groups," ed. H. Feuer, in "The Chemistry of Functional Groups," series ed. S. Patai, J. Wiley, New York, 1969, pp 613-684.

A-2. W.P. Norris, J. Org. Chem., 1960, 25, 1244.

A-3. O.A. Luk'yanov, N.M. Seregina, and V.A. Tartakovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1976, 225; Chem. Abstr., 1976, 84, 135574w.

A-4. Ref 1, pp 653, 654.

A-5. D.A. Cichra and H.G. Adolph, J. Org. Chem., 1982, 47, 2474. From the amine 7 hydrochloride the nitramine 3 (R = CH_3) (55%) was obtained.

A-6. W. Lijinsky, L.Keefer, E. Conrad, and R. Van de Bogart, J. Nat. Cancer Inst., 1972, 49, 1239.

A-7. P.A.S. Smith and R.N. Loeppky, J. Amer. Chem. Soc., 1967,

89, 1147.

A-8. Aldrich Chem. Co.

A-9. Organic Syntheses, III, 723.

A-10. J.H. Boyer, V.T. Ramakrishnan, T.P. Pillai and C.-B. Huang, Final Report April 1, 1979 to March 31, 1982 on Contract No. 0014-79-C-0353 to ONR.

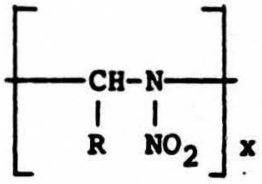
A-11. Triethyl and tri-n-butylamines were converted to corresponding dialkylnitrosamines by this mixture of nitric and hydrochloric acids in acetic anhydride (Y. Ogata, Y. Sawaki, and Y. Kuriyama, Tetrahedron, 1968, 1425).

A-12. Ref. 1, p 634.

A-13. Acetyl nitrate was produced *in situ* from acetic anhydride and nitric acid as reported by F.G. Bordwell and E.W. Garbisch, J. Am. Chem. Soc., 1960, 82, 3588.

A-14. Acetyl nitrite from silver acetate and nitrosyl chloride was recently reported (A.B. Kyte, R. Jones-Parry, and D. Whittaker, J. Chem. Soc. Chem. Commun., 1982, 74). Nitrite was detected in a preparation of acetyl nitrate from dinitrogen pentoxide and acetic anhydride (A.R. Cooksey, K.J. Morgan, and D.P. Morrey, Tetrahedron, 1970, 26, 5101.

B. α-Substituent in Nitramines. Except for gem-dinitramines 29,[1] the chemnistry of α-functional groups in nitramines is underdeveloped. A few examples e.g. 30,[1] described a nitramine with a tert-amino group attached to a primary α-carbon atom; however, with a sec-amino group an example was unstable on liberation from its nitrate salt 31,[1] and an α-primary aminonitramine 32 has not been reported.



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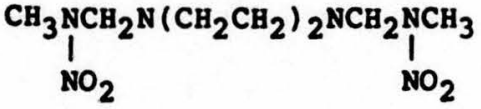

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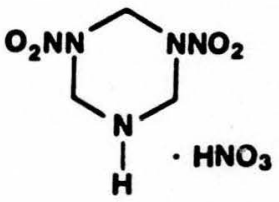

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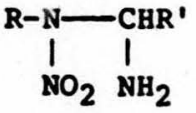

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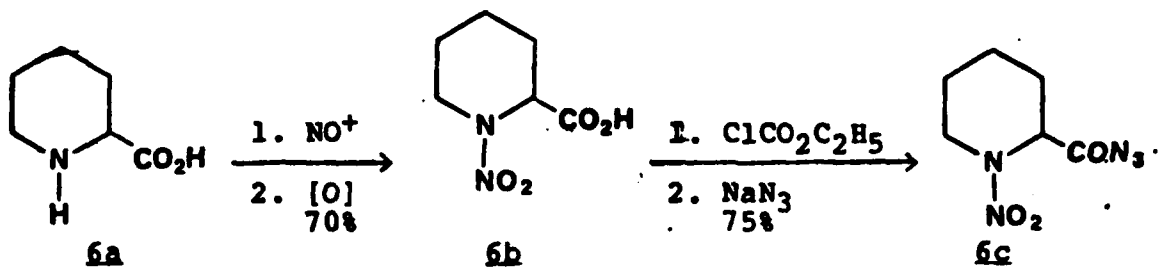
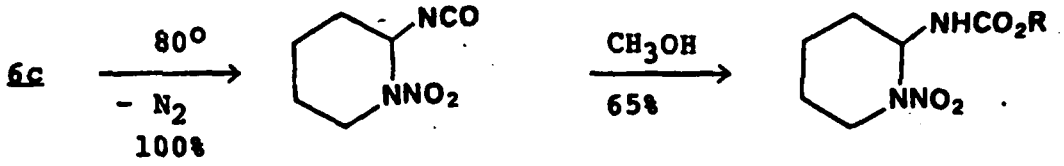
There are a few examples of nitramines with α-functions. α-Hydroxynitramines (unstable) and α-alkoxynitramines have been interconverted;[1] α-cyano,[1] α-chloro,[2,3] α-fluoro,[3] α-azido,[3] α-pyrazolo,[3] and α-nitraminoacids[4] have been reported.

When it became desirable to extend amine-carbonyl condensation to α-aminonitramines the initial problem of their preparation had to be solved. We have investigated a standard sequence of converting a carboxyl group to an amino group as is shown for the conversion of 1-nitropiperidine-2-carboxylic acid 6b to 1-nitro-2-aminopiperidine 6f isolated as the methyl carbamate derivative 6e (R = CH_3). Yields are shown for each conversion.



6a 6b 60% 6c 75%



6d 6e

Compounds 6c,d,e represent the first examples of nitramines with α-azidocarbonyl, α-isocyanato, and α-alkoxycarbonylamino functions.

An initial attempt to liberate the free amine 6f from its carbamate 6e (R = CH_3) under anhydrous conditions[5] gave instead the olefin 7 apparently by a spontaneous deamination of the amine 6f.

6f

7

Investigations are continuing.

Attempts to achieve α-functionalization in a secondary nitramine ($(RCH_2)_2NNO_2$) by metal interchange reactions failed when α-metallation could not be brought about.[6]

References

B-1. Ref A-1.

B-2. I.J. Shishkov, N.L Sadova, L.V. Vilkov, and V.P. Ivshin, Zh. Strukt. Khim., 1982, 23, 73; Chem. Abstr. 1982, 97, 215453p.

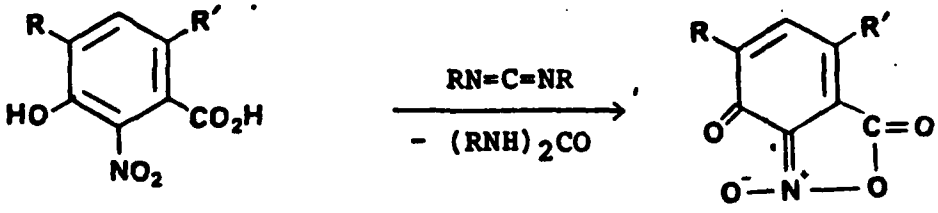
B-3. B. Unterhalt and F. Lieblein, Arch. Pharm., 1979, 312, 159.

B-4. H.T. Nagasawa, W.P. Muldoon, and F.N. Shirota, J. Med. Chem., 1977, 20, 1588.

B-5. This two step procedure with trimethylsilyl iodide followed by methanolysis has been reported: H.-J. Altenbach, B. Blech, J.A. Marco, and E. Vogel, Angew. Chem. Int. Ed. Engl., 1982, 21, 778.

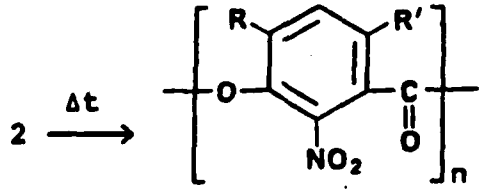
B-6. D. Siebach and D. ENders, Angew. Chem. Internat. Edit. Engl., 1975, 14, 15.

C. Cyclic Nitronic-Carboxylic Acid Anhydrides. Ring-opening polymerization has many practical applications, e.g., the conversion of caprolactam to nylon. A facile ring-opening polymerization of an isoxazolone-N-oxide was first encountered by Russian workers in attempts to transform derivatives of 2-nitro-3-hydroxybenzoic acid 33 into actinomycin analogs.[1] Dehydration converted the acid 33 to an isoxazolone-N-oxide 35 which thermally polymerized readily at ambient temperatures. Our investigations on similar converstions of 2,4,6-trinitro-3-hydroxybenzoic acid 34 to 9 are continuing.

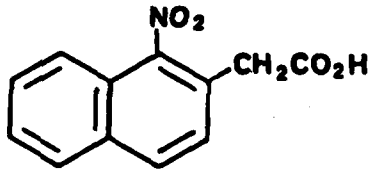


33 R = CH_3, R' = H
34 R = R' = NO_2

35 R = CH_3, R' = H



A review of the dehydration of 1-nitronaphthyl-2-acetic acid 36 is underway. A product 37 was reported in 1918.[2] We anticipate the collection of data to permit reassignment of the compound as an oxazinone-N-oxide 8.



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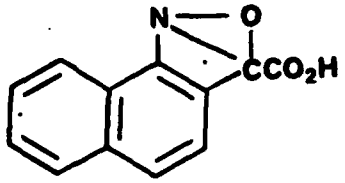

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References

C-1. B.V. Tsukerman, E.N. Glibin, and O.F. Ginzburg, Zh. Org. Khim., 1982, 18, 1721.

C-2. F. Mayer and T. Oppenheimer, Ber., 1918, 51, 510.

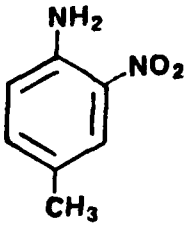
D. Products from Nitroform and Isocyanides. The project initiated by an undergraduate has been investigated further by Dr. Pillai.

In addition to the sydnone 13 (Ar = p-$O_2NC_6H_5$) the reaction between p-nitrophenyl isocyanide and nitroform also produced p-nitroaniline 38.

$$\underset{\text{Ar = p-}O_2NC_6H_4}{ArN^{+}\equiv C^{-}} \xrightarrow{HC(NO_2)_3} \underset{}{13} + \underset{38}{\text{p-}O_2NC_6H_4NH_2}$$

The similar reaction with p-tolyl isocyanide gave the sydnone 13 (Ar = p-$H_3CC_6H_5$) (needs to be confirmed) and 2-nitro-4-methylaniline.

$$\underset{\text{Ar = p-}H_3CC_6H_5}{ArN^{+}\equiv C^{-}} \xrightarrow{HC(NO_2)_3} \underset{}{13} + \underset{}{\text{2-nitro-4-methylaniline}}$$



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